Blow flies as remote sampling devices: Detection of insensitive munitions and their degradation products in the environment using LC-MS

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Overview

- Insensitive munitions (IM) are alternatives to traditional explosives that are less toxic and temperature sensitive, resulting in less unintentional detonations.
- Due to incomplete consumption in a blast, IMs are likely to deposit in the surrounding environment.
- IMs undergo abiotic, biotic, and UV-mediated transformation resulting in transformation products sometimes more toxic than the agent itself.
- This work aimed at using blow flies as environmental sampling devices for detecting insensitive munitions and their transformation products in the environment.

Methods

- LC-MS assay developed for a group of insensitive munitions and their degradation products.
- Trifluoromethane, XBridge BEH Amide column (2.1x100 mm) HPLC column.
- Hydrophilic interaction liquid chromatography (HILIC) mode of separation selected due to the polar nature of the analytes.
- Isocratic elution in 10 minutes using 95:5 acetonitrile/methanol/water with 10 mM ammonium acetate as the mobile phase.
- Q-Exactive Hybrid Quadrupole-Orbitrap mass spectrometer operated in Full MS using positive/negative polarity switching.
- Calibration curves made using calibrators ranging from 1 to 1250 ppb.
- Quality control samples (135 ppb) used for feeding experiments.
- Flies extracted using methanol sonication for 30 minutes.
- Following sonication, samples were centrifuged for 10 minutes.
- 75 μL of sample pipetted into autosampler vial and diluted with 225 μL of ACN.
- Injection volume was 2 μL and flow rate was 0.3 mL/min.

Feeding Experiments

- Adult blow flies undergoing feeding experiment. Each fly is maintained in an individual 1 oz. portion cup for 4 h with a small Timke placed in either water or IM.
- Flies exposed to each treatment were assayed into their respective cages for further monitoring.

Table 1. Select IM and IM transformation products detected in LC-MS/MS method

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Analyte Type</th>
<th>m/z</th>
<th>Retention</th>
<th>Mass Spectrometer</th>
<th>Avg.</th>
<th>Avg. LOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroguanidine</td>
<td>DNP</td>
<td>128.0986</td>
<td>2.72</td>
<td>Tetra</td>
<td>5.8956</td>
<td>6.4</td>
</tr>
<tr>
<td>2,4-dinitroaniline (2,4-DNAN)</td>
<td>DNP</td>
<td>166.0498</td>
<td>1.76</td>
<td>Tetra</td>
<td>5.8966</td>
<td>2.7</td>
</tr>
<tr>
<td>N,N-dimethyltoluidine (DDT)</td>
<td>DNP</td>
<td>115.0792</td>
<td>0.94</td>
<td>CO₂</td>
<td>5.8643</td>
<td>1.8</td>
</tr>
<tr>
<td>2,5-dimethyl-4-nitrophenol (2,5-DNP)</td>
<td>DNP</td>
<td>130.1354</td>
<td>3.27</td>
<td>CO₂</td>
<td>5.8683</td>
<td>16.4</td>
</tr>
<tr>
<td>2,4-diaminoanisole (2,4-DAA)</td>
<td>DNP</td>
<td>173.1150</td>
<td>1.22</td>
<td>CO₂</td>
<td>5.8683</td>
<td>16.4</td>
</tr>
<tr>
<td>2,5-dimethyl-4-nitrophenol (2,5-DNP)</td>
<td>DNP</td>
<td>130.1354</td>
<td>3.27</td>
<td>CO₂</td>
<td>5.8683</td>
<td>16.4</td>
</tr>
</tbody>
</table>

Conclusions & Future Work

- Developed a HILIC HPLC-MS method to retain IM compounds and their transformation products with LCQs at ng levels.
- Showed proof-of-concept studies detecting IMs and IM transformation products in fly matrix.
- C18 method developed for DNA separation and to improve NTO peak shape.
- Use DNA, NTO, and NQ for future feeding experiments such as longevity experiments at a variety of temperature and humidity conditions.
- Assess the detectability in environmental matrices such as different soil types.
- Identify IM transformation products due to fly metabolism of IM components.

References


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